

STUDIES OF CONCENTRATION AND TEMPERATURE DEPENDENCIES OF PRECIPITATION KINETICS IN IRON-COPPER ALLOYS USING KINETIC MONTE CARLO AND STOCHASTIC STATISTICAL SIMULATIONS

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Abstract – The earlier-developed *ab initio* model and the kinetic Monte Carlo method (KMCM) are used to simulate precipitation in a number of iron-copper alloys with different copper concentrations x and temperatures T . The same simulations are also made using the improved version of the earlier-suggested stochastic statistical method (SSM). The results obtained enable us to make a number of general conclusions about the dependencies of the decomposition kinetics in Fe-Cu alloys on x and T . We also show that the SSM describes the precipitation kinetics in a fair agreement with the KMCM, and employing the SSM in conjunction with the KMCM enables us to extend the KMC simulations to the longer evolution times. The results of simulations seem to agree with available experimental data for Fe-Cu alloys within statistical errors of simulations and the scatter of experimental results. Comparison of results of simulations to experiments for some multicomponent Fe-Cu-based alloys enables us to make certain conclusions about the influence of alloying elements in these alloys on the precipitation kinetics at different stages of evolution.

1 INTRODUCTION

Studies of the composition and temperature dependencies of the precipitation kinetics in alloys, in particular, in multicomponent Fe-Cu-based steels used in many industrial applications, attract great attention [1]-[11]. For such studies, it seems to be useful to have a reliable information about the similar dependencies for more simple, binary alloys treated as the reference systems. For example, discussing the precipitation kinetics in two Fe-Cu-based steels, NUCu-140 and NUCu-170, Kolli et al. [5, 6] compared their experimental results to those for several binaries Fe- x Cu with x between 1.34 and 1.5

at.%, while the two steels considered had notably different content of copper, 1.17 and 1.82%, respectively. As many characteristics of nucleation and growth, in particular, sizes and density of precipitates, strongly vary with $x = x_{\text{Cu}}$, such comparison can be not quite adequate. The precipitation characteristics can also significantly depend on temperature, while measurements of such dependencies, particularly for the nucleation stage, often meet difficulties [5, 6].

To obtain the quantitative information about the precipitation kinetics, particularly in the course of nucleation and growth, one can use simulations of these processes, if both the microscopic model and the methods of simulations used can be considered as reliable. For the Fe-Cu alloys, such reliable *ab initio* model has been developed by Soisson and Fu [9], and their detailed kinetic Monte Carlo simulations of nucleation and growth in the Fe-1.34Cu alloy at $T=773$ K revealed a good agreement with the available experimental data.

Therefore, the first aim of this work is to use the model and the kinetic Monte Carlo method (KMCM) developed in [9] to study the concentration and temperature dependencies of the precipitation kinetics in binary Fe-Cu alloys for a number of copper concentrations x and temperatures T , including those used by Kolli et al. [5, 6] for the NUCu steels. Comparison of results of these simulations to the available experimental data enables us to assess reliability of the Soisson and Fu model at different x and T , and also to discuss the differences in the precipitation kinetics between the Fe- x Cu binaries and the multicomponent Fe-Cu-based alloys with the same $x = x_{\text{Cu}}$ and T .

The second aim of this work is to discuss possible applications of the earlier-suggested stochastic statistical method (SSM) [13] for simulations of precipitation kinetics in those cases when the KMCM meets difficulties. Such difficulties arise, for example, in treatments of the coarsening stage or at relatively low temperatures $T \lesssim 300^\circ \text{C}$ (typical for service of many nuclear reactors) when the KMC simulations become time-consuming [9, 10]. Unlike the KMCM, the SSM allows parallelizing computer codes which can greatly accelerate computations, and this method seems also to be suitable for various generalizations, for example, for considerations of lattice misfit effects. However, in treatments of nucleation, some oversimplified models have been used in Ref. [13] which resulted in some fictitious breaks in simulated temporal dependencies. In this work we describe the improved version of the SSM free from these shortcomings and show that this version describes the main characteristics of nucleation, including the density and sizes of precipitates, in a good agreement with the KMCM. We also show that employing the SSM in conjunction with the KMCM enables us to extend the KMC simulations to the first stages of coarsening.

In Sec. 2 we briefly discuss the model, the alloy states and the methods used in our simulations. In Sec. 3 we describe the improved version of the SSM employed in this work. The results of our simulations are discussed and compared to the available experimental data in Sec. 4. The main conclusions are summarized in Sec. 5.

2 MODELS AND METHODS OF SIMULATIONS

For our simulations we use the *ab initio* model of Fe-Cu alloys developed by Soisson and Fu and described in detail in Refs. [9, 10, 13]. Here we only note that this model uses the following values of the binding energy between two copper atoms and between a copper atom and a vacancy, E_{CuCu}^{bn} and $E_{\text{Cu}v}^{bn}$, for the n -th neighbors (in eV):

$$\begin{aligned} E_{\text{CuCu}}^{b1} &= 0.121 - 0.182T, & E_{\text{CuCu}}^{b2} &= 0.021 - 0.091T, \\ E_{\text{Cu}v}^{b1} &= 0.126, & E_{\text{Cu}v}^{b2} &= 0.139. \end{aligned} \tag{1}$$

The high values of E_{CuCu}^{bn} correspond to the strong thermodynamic driving force for precipitation, while the strong attraction of a vacancy to copper atoms results in the strong vacancy trapping by copper precipitates discussed in detail in [9].

TABLE 1. The Fe- x Cu alloy states considered and parameters of “thermodynamic” critical embryos for these states calculated by method of Ref. [14].

Alloy state	T , K	x , at%	s	F_c/T	N_c^{th}	R_c^{th} , nm
A	773	1.17	0.247	5.58	15.4	0.353
B	773	1.34	0.285	4.38	14.3	0.344
C	773	1.82	0.393	2.30	12.2	0.326
D	713	1.34	0.352	2.47	10.7	0.312
E	663	1.34	0.425	1.36	8.2	0.286
F	561	0.78	0.387	1.11	5.3	0.247
G	873	1.15	0.163	12.6	28.3	0.433

The alloy states (below for short: states) used in our simulations are listed in Table 1. The degree of supersaturation for each of these states is characterized by the reduced supersaturation parameter s introduced in Refs. [13, 14]:

$$s(x, T) = [x - x_b(T)]/[x_s(T) - x_b(T)] \quad (2)$$

where the lower index s or b corresponds to the spinodal or the binodal. Values $s < 1$ correspond to the nucleation and growth evolution type, and $s > 1$, to spinodal decomposition.

The states A and C in Table 1 have the same temperature T and the copper content x as the above-mentioned steels NUCu-140 and NUCu-170 studied by Kolli et al. [5, 6]. For the states B and G , kinetics of precipitation under thermal aging was investigated in Refs. [1, 2, 3, 7], while for the state F , precipitation under neutron irradiation was studied by Miller et al. [4]. For the states D and E , experimental data about precipitation kinetics are unknown to us, and our simulations are made to study the temperature dependence of this kinetics.

In Table 1 we also present some parameters of the “thermodynamic” critical embryos for the states considered: the nucleation barrier F_c , the total number of copper atoms within the embryo, N_c^{th} , and the critical radius R_c^{th} defined as the radius of the sphere having the same volume as N_c^{th} copper atoms in the BCC lattice of α -iron with the lattice constant $a=0.288$ nm:

$$R_c^{th} = a(3N_c^{th}/8\pi)^{1/3} = 0.142(N_c^{th})^{1/3} \text{ nm}. \quad (3)$$

The characteristics of critical embryos shown in Table 1 and Fig. 1 are calculated by the statistical method of Dobretsov and Vaks [14] with the use of the *ab initio* model

Figure 1: (color online [17]). Concentration profiles $\Delta c(R) = c(R) - x$ in thermodynamic critical embryos for the alloy states considered, where $c(R) = c_{\text{Cu}}(r)$ is the mean copper concentration at the distance R from the center of embryo.

by Soisson and Fu [9] mentioned above and the pair cluster approximation which is typically highly accurate, particularly for dilute alloys, as both analytical studies [15] and comparisons with Monte Carlo simulations [16] show. Table 1 and Fig. 1 illustrate, in particular, the decreasing of the nucleation barrier F_c and the embryo size N_c^{th} with increasing supersaturation s . Table 1 also shows that for the given supersaturation s , lowering temperature T affects the critical embryo characteristics stronger than increasing concentration x [13]. As discussed below, the N_c^{th} and R_c^{th} values presented in Table 1 are usually close to those estimated in KMC simulations and in experiments.

Methods of both KMC and SSM simulations used in this work are described in detail in Refs. [9, 13]. Here we only mention some details of computations. For both the KMC and the SSM simulations we usually employed the simulation volume $V_s = (64a)^3$; for the state G with a low supersaturation we used the bigger $V_s = (128a)^3$. In our KMC simulations we usually followed $N_s^{KMC} \sim 10^{13}$ Monte Carlo steps, which at $V_s = (64a)^3$ took about five months on a standard workstation. The SSM simulations for $V_s = (64a)^3$ took usually about a month on a standard workstation (with no parallelization of codes made).

3 IMPROVEMENTS OF STOCHASTIC STATISTICAL METHOD

The original version of the SSM is described in Ref. [13]. To explain its improvements made in this work we first present the necessary relations from [13]. Evolution of a binary alloy is described by a stochastic kinetic equation written in the finite difference form for a short time interval δt :

$$\delta c_i \equiv c_i(t + \delta t) - c_i(t) = \delta c_i^d + \sum_{jnn(i)} \delta n_{ij}^f \quad (4)$$

where c_i is the occupation of site i by a minority (copper) atom averaged over some locally equilibrated vicinity of this site, and the “diffusional” term δc_i^d corresponds to the average atomic transfer for a certain effective direct atomic exchange (DAE) model:

$$\delta c_i^d \{c_k\} = \sum_{jnn(i)} M_{ij} 2 \sinh[\beta(\lambda_j - \lambda_i)/2] \delta t. \quad (5)$$

Here λ_i is the local chemical potential of site i given by Eq. (20) in [13], and M_{ij} is the generalized mobility:

$$M_{ij} = \gamma_{\alpha h}^{eff} b_{ij}^h \exp[\beta(\lambda_i + \lambda_j)/2]. \quad (6)$$

The factor b_{ij}^h in (6) is some function of local concentrations c_i given by Eq. (33) in [13], while $\gamma_{\alpha h}^{eff}$ is an effective rate of exchanges between neighboring minority and host atoms, α and h (copper and iron), which is proportional to the product of analogous rates $\gamma_{\alpha v}$ and γ_{hv} describing exchanges between a vacancy and an atom α and between a vacancy and an atom h , respectively:

$$\gamma_{\alpha h}^{eff} = \gamma_{\alpha v} \gamma_{hv} \nu(t). \quad (7)$$

Here the function $\nu(t)$ defined by Eq. (36) in [13] determines the “rescaling of time” between the original vacancy-mediated exchange model and the effective DAE model used for simulations. Temporal evolution of this DAE model is described by the “reduced time” t_r having the meaning of a mean number of atomic exchanges $\alpha \rightleftharpoons h$ for the physical time t . The reduced time t_r is related to this time t by the following differential or integral relations:

$$dt_r = \gamma_{\alpha h}^{\text{eff}} dt, \quad \gamma_{\alpha h}^{\text{eff}} = \gamma_{\alpha v} \gamma_{h v} \nu(t), \quad t = \int_0^{t_r} dt'_r / \gamma_{\alpha h}^{\text{eff}}(t'_r). \quad (8)$$

The form of the function $t(t_r)$ is discussed below. As mentioned in Ref. [18], Eqs. (4)–(8) can be derived not only for a simplified “quasi-equilibrium” model used in [13] that disregards renormalizations of effective interactions in a nonequilibrium alloy (whose importance for the diffusion kinetics was noted by Nastar et al. [19]) but also with allowing for these renormalizations.

The last term δn_{ij}^f in Eq. (4) is the fluctuative atomic transfer through the bond ij described by the Langevin-noise-type method: each δn_{ij}^f is treated as a random quantity with the Gaussian probability distribution:

$$W(\delta n_{ij}^f) = A_{ij} \exp[(-\delta n_{ij}^f)^2 / 2D_{ij}] \quad (9)$$

where A_{ij} is the normalization constant. The dispersion D_{ij} is related to the mobility M_{ij} and the time interval δt in Eq. (5) by the “fluctuation-dissipation” type relation:

$$D_{ij} = \langle (\delta n_{ij}^f)^2 \rangle = 2M_{ij} \delta t. \quad (10)$$

As discussed in detail in [13], for the non-equilibrium statistical systems under consideration, the Langevin-noise-type equations (4)–(10) should be supplemented by the “filtration of noise” procedure eliminating the short-wave contributions to fluctuations δn_{ij}^f as these contributions are already included in the diffusional term δc_i^d obtained by the statistical averaging over these short-wave fluctuations. Therefore, in the last term of Eq. (4), the full fluctuative transfer δn_{ij}^f should be replaced by its long-wave part δn_{ij}^{fc} . It can be made by introducing a proper cut-off factor $F_c(\mathbf{k})$ in the Fourier-component $\delta n_{f\alpha}(\mathbf{k})$ of the full fluctuation $\delta n_{ij}^f \equiv \delta n_{\alpha}^f(\mathbf{R}_{s\alpha})$ where $\mathbf{R}_{s\alpha}$ denotes the position of the ij bond center in the appropriate crystal sublattice α formed by these centers [12]:

$$\begin{aligned} \delta n_{ij}^f &\rightarrow \delta n^{fc}(\mathbf{R}_{s\alpha}) = \sum_{\mathbf{k}} \exp(-i\mathbf{k}\mathbf{R}_{s\alpha}) \delta n^f(\mathbf{k}) F_c(\mathbf{k}) \\ \delta n^f(\mathbf{k}) &= \frac{1}{N} \sum_{\mathbf{R}_{s\alpha}} \exp(i\mathbf{k}\mathbf{R}_s) \delta n^f(\mathbf{R}_{s\alpha}) \end{aligned} \quad (11)$$

where N is the total number of lattice sites (or atoms) in the crystal. The cut-off factor $F_c(\mathbf{k})$ for the BCC lattice can be taken in the Gaussian-like form:

$$F_c^{\text{BCC}}(\mathbf{k}) = \exp[-4g^2(1 - \cos \varphi_1 \cos \varphi_2 \cos \varphi_3)] \quad (12)$$

where $\varphi_\nu = k_\nu a/2$; k_ν is the vector \mathbf{k} component along the main crystal axis ν ; and a is the BCC lattice constant. At large $g^2 \gg 1$, the expression (12) is reduced to a Gaussian $\exp(-k^2 l^2/2)$ with $l = ga$. Therefore, the reduced length $g = l/a$ characterizes the mean size of locally equilibrated subsystems.

Figure 2: (color online [17]). Evolution of the free energy per copper atom, $F(t_r)$ (a), and the density $d_p(t_r)$ of supercritical precipitates or their total number $N_p(t_r)$ within simulation volume $V_s = (64a)^3$ (b), obtained for the state *A* in the SSM simulations with different g_0 and t_0 . Curves 1, 2, and 3 (red, green and blue online [17]) correspond to $t_0 = 40$ and $g_0 = 1.4, 1.35$, and 1.45 , respectively. Curves 4 and 5 (red on-line) correspond to $g_0 = 1.4$ and $t_0 = 50$ and 30 , respectively. Thin vertical line corresponds to $t_{rN} = 18$.

This size, generally, varies with the aging time t or t_r . In particular, after creation of a supercritical precipitate, the degree of local equilibrium in the adjacent region should increase with respect to other regions where such precipitates are not born yet. Therefore, after completion of nucleation at some reduced time t_{rN} (which can be estimated as the time for which the density of precipitates reaches its maximum), the alloy should rapidly approach the two-phase equilibrium, and the length $l = ga$ should become large, which should lead to a sharp decrease of the fluctuative terms $\delta n^f = \delta n^{fc}$ in Eqs. (11) and (4).

To describe this physical picture with the minimal number of model parameters, the time dependence $g(t_r)$ was approximated in [13] by a simple one-parametric expression (71) with a break at $t_r = t_{rN}$. In the present work we use for $g(t_r)$ a smooth two-parametric expression:

$$g(t_r) = g_0(1 + t_r^2/t_0^2) \quad (13)$$

where g_0 and t_0 have the order of magnitude of the reduced critical radius R_c/a and the reduced nucleation time t_{rN} , respectively.

TABLE 2. Parameters g_0 and t_0 in (13), reduced nucleation time t_{rN} , and maximum precipitate density d_{max} (in 10^{24} m^{-3}) for the alloy states considered.

Alloy state	g_0	t_0	t_{rN}	d_{max}^{SSM}	d_{max}^{KMC}
<i>A</i>	1.4	40	~ 20	3.4	4.0
<i>B</i>	1.4	30	~ 20	5.4, 5.8	6.1
<i>C</i>	1.45	20	~ 10	14.9	14.2
<i>D</i>	1.4	10	~ 10	9.7	10.1
<i>E</i>	1.6	10	~ 10	13.6	11.2
<i>F</i>	1.6	5	~ 5	9.9	8

To estimate values g_0 and t_0 within the SSM, we can use the “maximum thermodynamic gain” principle discussed in detail in [13]: we suppose that the “most realistic” values of these parameters correspond to the minimum of the free energy of an alloy after completion of nucleation. To illustrate this variational method of estimating g_0 and t_0 , in Fig. 2 we present the SSM-simulated temporal dependencies of the free energy per copper atom for the state *A* in Table 1 at several g_0 and t_0 close to their “optimal” values. The free energy $F = F(c_i)$ was calculated according to Eq. (24) in [13] with the simulated $c_i = c_i(t_r)$ dependencies. For simplicity, the initial state was taken uniform:

Figure 3: (color online [17]). Evolution of the density of precipitates, $d_p(t_r)$ (a), and their mean radius $R(t_r)$ (b) obtained in the SSM simulations for the state *A* in Table 1. Dotted vertical lines correspond to the values t_{ir} in Eqs. (16).

$c_i(0) = c = \text{const}$, thus the initial increase of F at $t_r \lesssim 0.3 t_{rN}$ seen in Fig. 2a is related just to switching-on fluctuations at $t_r = 0$. Fig. 2a shows that the influence of this spurious increase of F ceases only at $t_r \gtrsim 2t_{rN}$, while at too long $t_r \gtrsim 4t_{rN}$, the fluctuations are effectively switched-off according to Eqs. (11)-(13). Therefore, to estimate parameters g_0 and t_0 , we usually consider the interval $2t_{rN} \gtrsim t_r \gtrsim 4t_{rN}$. For the most of states considered, the free energy $F(t_r)$ has here a distinct minimum with respect to g_0 and t_0 , as illustrated by Fig. 2a. Fig. 2b illustrates sensitivity of the precipitate density d_p to the choice of g_0 and t_0 . The resulting scatter in simulated $d_p(t_r)$ usually lies within statistical errors of simulations.

In Table 2 we present the values of g_0 and t_0 in (13) estimated as described above. For the state *G* the simulations are time-consuming, thus such estimates have not been made in this work. To assess adequacy of our SSM simulations, in the two last columns of Table 2 we compare the values of the maximum density d_{max} of supercritical precipitates obtained in the SSM simulations to those obtained in the KMC simulations. For the state *B* in Table 2, two values d_{max}^{SSM} correspond to the two simulations (shown in Fig. 6) with the different random number sets. We see that the SSM and the KMC results for d_{max} agree within statistical errors of simulations.

The precipitation kinetics is usually characterized by the density and the mean radius of supercritical precipitates, $d_p(t)$ and $R(t)$, defined by the following relations:

$$\begin{aligned} d_p(t) &= \sum_k \nu_k(t) / V_s, \\ R(t) &= \sum_k \nu_k(t) R_k / \sum_k \nu_k(t). \end{aligned} \quad (14)$$

Here $\nu_k(t)$ is the number of clusters containing k copper atoms, V_s is the simulation volume, R_k is defined similarly to Eq. (3): $R_k = a(3k/8\pi)^{1/3}$, and sums over k in (14) include only clusters with $k \geq N_c$ where N_c is the “critical” size chosen. As discussed in [9, 13] and below, the exact choice of this size (if reasonable) usually does not significantly affect the $d_p(t)$ and $R(t)$ values in (14). Therefore, we take N_c close to its “thermodynamic” value N_c^{th} in Table 1 putting $N_c=15, 15, 12, 11, 8, 5$ and 28 copper atoms for the state *A, B, C, D, E, F* and *G*, respectively. Temporal dependencies $d_p(t_r)$ and $R(t_r)$ obtained in our SSM simulations with such N_c are illustrated by Fig. 3 for the state *A*; for the rest states considered, these dependencies are similar. Fig. 3 illustrates the sequence of four well-defined stages of precipitation accepted in the classical theory of nucleation (see, e. g., [20]): incubation, nucleation, growth and coarsening, as well as the presence of an “intermediate” stage between growth and coarsening (seen also in the simulations of Soisson and Martin [20] and discussed in detail by Barashev et al. [21]) which corresponds to the beginning of Ostwald ripening when the bigger precipitates already start to grow due to dissolving the smaller ones but the latter do not disappear yet. For brevity, this intermediate stage will be called “pre-coarsening”.

Let us now discuss the “rescaling of time” function $t(t_r)$ in Eq. (8) determined by the temporal dependence of the effective direct exchange rate $\gamma_{ah}^{eff} = \gamma_{CuFe}^{eff}(t_r)$. For simplicity, this dependence was approximated in [13] by a simple two-parametric expression (77) which included sharp breaks at some t_r . More adequate interpolations for $t(t_r)$ can be

obtained from comparison of the SSM and the KMC results for the density and the mean size of precipitates, that is, from an approximate solution of two equations:

$$d_p^{KMC}(t) = d_p^{SSM}(t_r), \quad R_{KMC}(t) = R_{SSM}(t_r). \quad (15)$$

Our estimates of functions $t(t_r)$ for which both equations (15) are satisfied with a reasonable accuracy showed that for all alloy states considered, these functions have a similar form characterized by the presence of four intervals of t_r with an approximately constant value of the derivative $D = d \ln t / d \ln t_r \propto 1/\gamma_{CuFe}^{eff}$ within each interval. These intervals (i) are determined by the inequalities:

$$\begin{aligned} (1) \quad & t_r < t_{r1}, & (2) \quad & t_{r1} < t_r < t_{r2}, \\ (3) \quad & t_{r2} < t_r < t_{r3}, & (4) \quad & t_{r3} < t_r, \end{aligned} \quad (16)$$

where the point t_{r1} , t_{r2} or t_{r3} approximately separates the stages of nucleation and growth, growth and pre-coarsening, or pre-coarsening and coarsening, respectively, as illustrated by Fig. 3. Therefore, within each interval (i) we use a simple power interpolation

$$t = A_i t_r^{D_i} \quad (17)$$

with the values of parameters t_{ri} , D_i and A_i given in Table 3. For the state F with a relatively low $T = 561$ K, our KMC simulations (illustrated by Fig. 11 below) are time consuming and reach only the growth stage, thus the interpolation (17) has not been constructed for this state.

Functions $t(t_r)$ obtained are shown in Fig. 4. To compare the precipitation parameters at different temperatures T for which the equilibrium vacancy concentration $c_v^{eq}(T)$ can be very different, in Fig. 4 we use the “scaled” time $t_s(t_r)$ defined as

$$t_s(t_r) = t(t_r) c_v^{eq}(T) / c_v^{eq}(773 \text{ K}), \quad (18)$$

to cancel the standard scaling factor $1/c_v^{eq}$ in the t_s value. For the $c_v^{eq}(T)$ we use the Soisson and Fu estimate [9]:

$$c_v^{eq}(T) = \exp(-\varepsilon_v^{for}/T), \quad \varepsilon_v^{for} = 2.18 \text{ eV}. \quad (19)$$

The SSM values $d_p^{SSM}(t)$ and $R_{SSM}(t)$ found using Eqs. (17) and Table 3 are compared to the appropriate KMC results in Figs. 5-10. Note that the interpolation (17) includes some minor breaks at points $t_r = t_{ri}$ which are seen in Fig. 4. These breaks can be removed by introducing some smooth matching of two lines (17) adjacent to each point t_{ri} , which also leads to the better agreement between the SSM and the KMC results in Figs. 5-10. However, to avoid introducing too many interpolation parameters, in this work we use a more simple interpolation (17) which seems to provide a sufficiently adequate description of precipitation.

As discussed in Ref. [13], the significant changes of derivatives $D_i \sim 1/(\gamma_{CuFe}^{eff})_i$ between different intervals i seen in Fig. 4 can be related to the strong vacancy trapping by copper precipitates and to the changes of scale of this trapping in the course of precipitation. In particular, the relatively low values of derivatives D_3 for the pre-coarsening stage can be related to the strong vacancy trapping for this stage (illustrated by Fig. 6a in [9]) which should result in a sharp increase of the effective rate γ_{CuFe}^{eff} in Eq. (8) [13]. Note also similarity of the curves $t_s(t_r)$ for different alloy states in Fig. 4, as well as rather smooth variations of parameters D_i and A_i in Table 3 under changes of concentration

Figure 4: (color online [17]). The scaled physical time $t_s(t_r)$ defined by Eqs. (17) and (18) versus the reduced time t_r . Each curve corresponds to the alloy state indicated by a symbol near this curve.

x and temperature T corresponding to these different states. It seems to reflect a great similarity of the vacancy trapping effects within each interval i considered for the different alloy states. This similarity can be used for various SSM-based extrapolations of KMC simulations, in particular, for the SSM-based simulations of precipitation in Fe-Cu alloys at most different concentrations x and temperatures T with the use for the parameters t_{ri} , D_i and A_i in Eqs. (16) and (17) some interpolations between their values presented in Table 3. This similarity is also used for the extrapolations of KMC simulations to the first stages of coarsening discussed below.

TABLE 3. Values of parameters t_{ri} , D_i and A_i (in hours) in Eqs. (16) and (17).

Alloy state	t_{r1}	t_{r2}	t_{r3}	D_1	D_2	D_3	D_4	A_1	A_2	A_3	A_4
<i>A</i>	18	506	5500	0.7	0.23	0.04	0.3	0.061	0.24	0.77	0.08
<i>B</i>	7.4	192	7240	1.1	0.33	0.11	0.4	0.021	0.097	0.30	0.023
<i>C</i>	2.9	70	3000	1.85	0.23	0.12	0.35	0.013	0.071	0.11	0.018
<i>D</i>	5	60	2300	1	0.23	0.08	0.27	0.027	0.14	0.26	0.026
<i>E</i>	3.2	60	2200	1.5	0.19	0.08	0.3	0.015	0.16	0.25	0.012

To conclude this section we note that the simplified treatment of fluctuations based on Eqs. (9)-(13) can adequately describe nucleation and growth only when these two processes are sufficiently separated from each other, so that switching off fluctuations after completion of nucleation implied by Eq. (13) can be appropriate. Figs. 5-10 show that this condition is more or less satisfied for the first five states in Table 1. At the same time, for the states *F* and *G*, that is, at low temperatures $T \lesssim 300^\circ \text{C}$ or at low supersaturations $s \lesssim 0.2$, the nucleation, growth and pre-coarsening stages overlap very strongly, as Figs. 11, 12 and 17 show, and the simple model (9)-(13) implying the type of evolution shown in Fig. 3 can hardly be adequate. Therefore, for the states *F* and *G*, only KMC simulations are presented in the present work. Further refinements of the SSM are evidently needed to employ this method at the low temperatures or low supersaturations mentioned.

4 RESULTS OF SIMULATIONS AND COMPARISON WITH EXPERIMENTS

The results of our simulations together with the available experimental data for some Fe-Cu and Fe-Cu-based alloys are presented in Figs. 5-17. Figs. 5-12 show the temporal evolution of the density and the mean radius of precipitates, $d_p(t)$ and $R(t)$. Note that for

Figure 5: (color online [17]). Evolution of the density of precipitates, $d_p(t)$ (top figure), and their mean radius $R(t)$ (bottom figure) obtained in our simulations for the state A with $x=1.17$ (in at.%, here and below), $T=773$ K for the critical size $N_c = 15$ copper atoms. Right scale shows the number of precipitates within simulation volume $V_s = (64a)^3$. Solid curves correspond to the KMCM, and dashed curves, to the SSM. Points show experimental data by Kolli et al. [6] for the multicomponent steel NUCu-140 with the same $x_{Cu}=1.17$ and $T=773$ K for $N_c = 11$.

Figure 6: (color online [17]). The same as in Fig. 5 but for the state B with $x=1.34$, $T = 773$ K for $N_c = 15$. Two dashed curves (red and green on-line) correspond to the two SSM simulations with different random number sets. Symbols correspond to experimental data for the state B : circles, to [1]; triangles, to [2]; and rhombus, to [3].

the state F in Fig. 11, this evolution is described in terms of the scaled time t_s defined by Eq. (18) (with replacing $t_r \rightarrow t$), as the equilibrium vacancy concentration $c_v^{eq}(T)$ at the low $T=561$ K considered is negligibly small, while actually (in particular, in experiments [4]) the precipitation at such low T occurs only in irradiated materials where the vacancies (together with the interstitial atoms) are formed due to irradiation.

Figs. 13-16 illustrate the concentration and temperature dependencies of the maximum precipitate density $d_p^{max} = d_{max}$, as well as of some temporal characteristics of precipitation, t^{max} , t^c and $t^{c,0.1}$, defined by the relations:

$$d_p(t^{max}) = d_{max}, \quad (20)$$

$$t^c = t(t_{r3}), \quad (21)$$

$$d_p(t^{c,0.1}) = 0.1 d_{max} \quad (22)$$

where the reduced time t_{r3} and the function $t(t_r)$ in (21) are the same as in Eqs. (16) and (17). The time t^{max} usually corresponds to the completion of nucleation or beginning of growth; the time t^c approximately corresponds to the onset of coarsening, and $t^{c,0.1}$ can characterize the time of completion of the first stage of coarsening and beginning of its more advanced stages. For brevity, t^{max} will be called the “nucleation time”, and $t^{c,0.1}$, the “advanced coarsening time”. In Figs. 13-16 we also present the experimental estimates of t^{max} and $t^{c,0.1}$ but not t^c as such estimates are usually not certain for the onset of coarsening.

Fig. 17 illustrates temporal evolution of the precipitate size distributions observed in our simulations. In caption to this figure we use the times $t^{N,\alpha}$ and $t^{c,\alpha}$ defined similarly to the “nucleation time” t^{max} and the “advanced coarsening time” $t^{c,0.1}$ in Eqs. (20) and (22):

$$d_p(t^{N,\alpha}) = \alpha d_{max}, \quad t^{N,\alpha} < t^{max}, \quad (23)$$

$$d_p(t^{c,\alpha}) = \alpha d_{max}, \quad t^{c,\alpha} > t^{max} \quad (24)$$

where the number α is less than unity. Times $t^{N,\alpha}$ qualitatively correspond to the nucleation stage, and $t^{c,\alpha}$, to the coarsening stage.

Let us discuss the results presented in Figs. 5-17. First, Figs. 5-12 and 17 show that the above-mentioned strong attraction between a vacancy and a copper atom leads to a great difference in the precipitation kinetics between iron-copper alloys and alloys with no such attraction, such as the alloys described by simplified models with time-independent

Figure 7: (color online [17]). The same as in Fig. 6 but for seven different KMC simulations for $N_c = 10$. Thick solid line (red on-line) corresponds to the same KMC simulation as that shown in Fig. 6 by thick line for the choice $N_c = 15$.

Figure 8: (color online [17]). The same as in Fig. 5 but for the state C with $x=1.82$, $T = 773$ K for $N_c = 12$. Points show experimental data by Kolli et al. [5, 6] for the multicomponent steel NUCu-170 with the same $x_{Cu} = 1.82$, $T = 773$ K for $N_c = 11$.

effective direct exchange rates γ_{ah}^{eff} in (8) for which this kinetics is illustrated by Fig. 3, or the models with a relatively weak vacancy-minority atom interaction for which this kinetics is illustrated by Fig. 1 in [20] or Fig. 4 in [21]. For such simplified models, the presence of five well-defined stages of evolution shown in Fig. 3 is characteristic, including the distinct pre-coarsening stage mentioned above. On the contrary, in Figs. 5-12 such an intermediate pre-coarsening stage is not seen, the “pure nucleation” and “pure growth” stages are relatively short (if exist at all), and the nucleation, growth and pre-coarsening stages significantly overlap each other. It is also illustrated by the size distribution functions $\nu_k(t)$ in Fig. 17 which seem to imply that the nucleation, growth and pre-coarsening processes at $0.5 t^{max} \lesssim t \lesssim t^{max}$ occur simultaneously. As discussed in [13], these kinetic features seem to be mainly related to the strong vacancy trapping by copper precipitates, which leads to a great acceleration of both the growth and the Ostwald ripening processes as compared to the alloys with no such trapping.

Figs. 5-10 also show that the simplified direct-atomic-exchange model (4)-(12) using the above-mentioned maximum thermodynamic gain principle and the simple interpolation (17) describes the precipitation kinetics in a fair agreement with the KMCM. Discrepancies between the SSM and the KMCM results lie usually within statistical errors of simulations, and these discrepancies can be still more reduced if the smoothed interpolations mentioned above are used instead of more simple expressions (17).

Figs. 5, 6 and 8-10 also illustrate opportunities to use the SSM to extrapolate the KMC simulations to the longer evolution times. As mentioned, the KMC simulations of coarsening are time-consuming, unlike the SSM simulations. At the same time, the above-described considerations about the physical nature of the “rescaling of time” function $t(t_r)$ in (17) enable us to expect that this function preserves its form for the first stages of coarsening at least up to $t \sim t^{c,0.1}$, until the later, more advanced stages of coarsening (including the asymptotic Lifshits-Slyozov-Wagner stage [22, 23]) start. Therefore, we can use the SSM simulated $d_p(t_r)$, $R(t_r)$ and Eq. (17) to estimate the $d_p(t)$ and $R(t)$ values for those t for which the KMC results are not available. This is shown in Figs. 5, 6 and 8-10.

Figs. 6 and 7 also illustrate some methodical points. Two dashed curves in Fig. 6 (red and green on-line) correspond to two SSM simulations with the different random number sets, thus their difference illustrates the statistical scatter of the SSM simulation results. We see that this scatter is significant only at the very end of simulations when the total precipitate number N_p becomes small. Similarly, seven different KMC simulations shown in Fig. 7 illustrate the statistical scatter of the KMC simulation results. Influence of the choice of the “critical” size N_c in Eqs. (14) on the simulated $d_p(t)$ and $R(t)$ is illustrated by Figs. 6 and 7 which correspond to the same alloy state B but to the different N_c , 15 and 11 copper atoms, respectively, while the thick solid curve in both Fig. 6 and Fig. 7 (red on-line in Fig. 7) corresponds to the same KMC simulation. We see that the variations of N_c used make noticeable effects on the simulated $d_p(t)$ and $R(t)$ only at the

Figure 9: (color online [17]). The same as in Fig. 5 but for the state D with $x=1.34$, $T = 713$ K for $N_c = 11$.

Figure 10: (color online [17]). The same as in Fig. 5 but for the state E with $x=1.34$, $T = 663$ K for $N_c = 8$.

first stages of nucleation, while later on such effects become insignificant.

Let us discuss the concentration and temperature dependencies of the kinetic characteristics of precipitation presented in Figs. 13-16. For the maximum precipitate density d_{max} , these dependencies shown in Figs. 13 and 15 are mainly determined by the reduced supersaturation s (defined in Eq. (2) and Table 1) which characterizes the scale of the thermodynamic driving force for precipitation. For the given temperature T or the given concentration x , the d_{max} value increases with s , and at low $s \lesssim 0.3$ or high $T \gtrsim 800$ K this rise is rather sharp. At the same time, Fig. 15 shows that at not low $s \gtrsim 0.3 - 0.4$ and not high T , the d_{max} value changes with T more slowly, and at $T \lesssim 700$ K, the further lowering temperature makes little effect on the d_{max} . It may imply that the slowing down of kinetics due to the strong vacancy-copper atom correlations discussed below becomes important for these T . The temporal characteristics of precipitation shown in Figs. 14 and 16b decrease with increasing supersaturation s , which can be explained by an increase of the thermodynamic driving force. At the same time, Fig. 16a shows that at not low $s \gtrsim 0.3 - 0.4$ and not high $T \lesssim 750$ K, the scaled times t_s^{max} , t_s^c and $t_s^{c,10}$ vary with temperature rather weakly. It can be explained by an interplay between an increase with lowering T of both the thermodynamic driving forces which promote the evolution, and the vacancy-copper atom correlations which reduce the copper diffusivity D_{Cu} [9] and thereby slow down the evolution.

Let us discuss the precipitate size distributions $\nu_k(t)$ shown in Fig. 17. First, we see that these distributions are usually rather broad, and sizes of different precipitates are typically very different. Therefore, characterization of these sizes by only their mean value $R(t)$ used in Figs. 5-12 is oversimplified and incomplete. It is true not only for the coarsening stage (for which a great difference in the precipitate sizes is natural as the bigger precipitates coarsen due to dissolving the smaller ones) but also for all other stages of precipitation. It can be related to the strong overlapping of the nucleation, growth and pre-coarsening stages mentioned above. Comparison of the size distributions $\nu_k(t)$ at $t=t^{max}$ and $t=1.1 t^{max}$ (that is, frames G2 and G3, B2 and B3, or D2 and D3 in Fig. 17) also illustrates the significant overlapping of growth and early coarsening stages. We see that the great majority of precipitates at $t=1.1 t^{max}$ still continue to grow due to the absorption of copper atoms from the matrix, even though some smallest precipitates already start to dissolve. Such significant overlapping of growth and early coarsening stages agrees with the observations by Mathon et al. for the Fe-1.34Cu alloys (the state B in Table 1) [3], and it was also noted by Kolli et al. for the NUCu steels [6]. Second, the comparison of the size distributions $\nu_k(t)$ at $t=t^{max}$ and $t=1.1 t^{max}$ also illustrates very sharp variations of these distributions with the evolution time t , in particular, at t corresponding to the beginning of coarsening, which is not clearly seen in the “averaged” description of Figs. 5-12. Third, Fig. 17 shows that the precipitate size distribution $\nu_k(t)$ for the state G with the highest temperature $T=873$ K is, generally, much more uniform than $\nu_k(t)$ for the states B and D with the lower $T=773$ K and 713 K, particularly for the early coarsening stage, which is illustrated by frames G4, B4 and D4. In particular, in frames B4 and D4 we observe only one very big cluster with $k \sim 600$ copper atoms,

Figure 11: The same as in Fig. 5 but for the state F $x=0.78$, $T = 561$ K for $N_c = 5$.

Figure 12: The same as in Fig. 5 but for the state G with $x=1.15$, $T = 873$ K for $N_c = 28$. Solid symbols show experimental data by Shabadi et al. [7] for the following alloys aged at $T = 873$ K: circles, binary Fe-1.15Cu; squares, ternary Fe-1.14Cu-0.99Mn. Right scale shows the number of precipitates, N_p , within simulation volume $V_s = (128a)^3$.

numerous small clusters with $k < 200$ copper atoms, and 3-4 “middle-sized” clusters with $k \sim 200-300$ atoms (the same features are also observed in $\nu_k(t)$ for the state A not shown in Fig. 17 on considerations of space), in the great difference with frame G4 (as well as G2 and G3) where the cluster size distribution is rather uniform. This difference can be related to the weakening of the vacancy-copper atom correlations at high T which can enhance the copper diffusivity D_{Cu} and thereby promote growth of many big precipitates for the state G unlike the states A , B and D , but these points need further studies. Finally, the lower row of Fig. 17 illustrates features of precipitation at low temperatures $T \sim 300^\circ$ C when the vacancies (necessary for the atomic diffusion) are provided by irradiation. Figs. F1–F3 illustrate a very strong overlapping of the nucleation growth and pre-coarsening stages, while the coarsening stage was not reached in these our simulations.

Let us now compare the simulation results to the available experimental data. For the state B and the KMC simulations shown in Figs. 6 and 7 by thick lines, the detailed comparison with various experiments was given by Soisson and Fu [9] who concluded that the predictions of simulations are reliable. The results presented in Figs. 6, 7, 14 and 16 can complement their discussion by the two points. First, Figs. 6 and 7 confirm that the disagreements between simulations and experimental observations seem usually to lie within statistical errors of simulations and the scatter of experimental results. Second, Figs. 6, 14 and 16 show that the SSM-based extrapolations of KMC simulations for the first stages of coarsening seem to agree with the observations as well.

For the state G with $x = 1.15$, $T = 873$ K, our simulations are compared to the data by Shabadi et al. [7] in Fig. 12. As supersaturation s and the precipitate density d_p for this state are rather low, these simulations are time-consuming and include only nucleation and growth stages, while the data by Shabadi et al. seem to correspond to the longer aging times and have significant errors. Within these errors, the simulation and experimental results in Fig. 12 can be considered as agreeing with each other, particularly for the maximum precipitate density d_{max} , though the simulated evolution times can be somewhat shorter than the observed ones. Solid squares in Fig. 12 correspond to a ternary Fe-Cu-Mn alloy and illustrate the effect of the third alloying element Mn on the precipitation kinetics. The presence of Mn seems to lead to an increase of the maximum precipitate density d_{max} by about twice with respect to the analogous Fe-Cu binary, in a qualitative contrast with the effect of alloying elements on the d_{max} value in the NUCu steels discussed below.

Figure 13: Concentration dependence of the maximum density of precipitates, d_{max} , for decomposition of Fe- x Cu and Fe-Cu-based alloys at $T = 773$ K. Open symbols here and below correspond to our simulations, and solid symbols, to experiments. Solid circle corresponds to experiments [2] for the state B , while solid square and solid triangle, to experiments [5, 6] for the multicomponent steel NUCu-140 with $x_{Cu}=1.17$ and NUCu-170 with $x_{Cu}=1.82$, respectively. Dashed lines here and below are given to guide the eye.

Figure 14: Concentration dependence of temporal characteristics of precipitation: t^{max} (circles), t^c (triangles), and $t^{c,0.1}$ (squares), defined in the text by Eqs. (20), (21) and (22), respectively, at $T = 773$ K. Solid circle and solid square at $x_{Cu}=1.17$ or $x_{Cu}=1.82$ correspond to the data [5, 6] for the steel NUCu-140 or NUCu-170, respectively, while solid circle and solid square at $x=1.34$ correspond to the data [1]-[3] for the state B.

Figure 15: Temperature dependence of the maximum density of precipitates in the course of decomposition of Fe- x Cu and Fe-Cu-based alloys. Open circles correspond to the states B, D and E with $x=1.34$; open square, to the state A with $x=1.17$; and open triangle, to the state G with $x=1.15$. Solid circle corresponds to experiments [2] for the state B with $x=1.34$; solid square, to experiments [6] for the steel NUCu-140 with $x_{Cu}=1.17$; and solid triangle, to experiments [7] for the state G with $x=1.15$.

In Figs. 5, 8, and 13-16 we compare the simulation results for the state A or C with $T = 773$ K and $x = 1.17$ or 1.82 to the data by Kolli et al. [5, 6] for the multicomponent steels NUCu-140 and NUCu-170 with the same T and x_{Cu} . In addition to copper, these steels contain a number of alloying elements: C, Al, Ni, Si, Mn, Nb, P and S, 5.49% on the total in NUCu-140, and 5.83%, in NUCu-170, while the partial concentrations of each alloying element in these two steels are very close to each other [5, 6]. Therefore, differences in the precipitation kinetics for these two steels can be mainly related to the difference in the copper content x_{Cu} . Then comparison of this kinetics for each of these steels to that for the analogous binary Fe- x Cu alloy can elucidate the effect of alloying elements on the precipitation at different x_{Cu} . Qualitatively, these problems were discussed by Kolli et al. [6]. Our simulations enable us to consider these points quantitatively. Let us also note that the critical sizes N_c for these two steels estimated by Kolli et al. [5, 6]: $N_c \simeq 11$ copper atoms, are rather close to the estimates for their binary analogues presented in Table 1: $N_c^{th}(A) \simeq 15$, $N_c^{th}(C) \simeq 12$ copper atoms.

Let us first discuss the nucleation and growth stages illustrated by Figs. 5 and 8. For the NUCu-140 or NUCu-170 steel this corresponds to $t \lesssim 1$ h and $t \lesssim 0.25$ h, respectively, and the maximum precipitate density d_{max} in each steel is lower than that in its binary analogue by about three times. However, for the NUCu-140, both the values and the temporal dependencies of $d_p(t)$ and $R(t)$ in Fig. 5 seem to not greatly differ from those simulated for the Fe-1.17Cu alloy, particularly for the nucleation stage, and the nucleation time t^{max} can be similar, too. On the contrary, for the NUCu-170, the data at $t=0.25$ h shown in Fig. 8, particularly for the $R(t)$ value, sharply disagree with those simulated for the Fe-1.82Cu alloy, while the nucleation time t^{max} exceeds that for the Fe-1.82Cu alloy by an order of magnitude.

Therefore, our comparison seems to imply that the effect of almost the same content of alloying elements on the nucleation kinetics in NUCu-170 with the higher copper content $x_{Cu}=1.82$ is much stronger and qualitatively different from that in NUCu-140 with the lower $x_{Cu}=1.17$. Physically, such conclusion does not seem to be natural. In this connection we note that this conclusion is mainly based on the data for the mean precipitate size in NUCu-170 at $t=0.25$ h reported by Kolli and Seidman [5]: $R \simeq 1.2$ nm. This value much exceeds the critical radius $R_c \simeq 0.3$ nm estimated for this steel in [5]: $R \simeq 4R_c$. It should imply that in the course of the nucleation stage (supposed in [5] for the NUCu-170 at $t=0.25$ h to explain a steep rise of the precipitate density $d_p(t)$ between $t=0.25$ h and $t=1$ h seen in Fig. 8) the new-born precipitates grow extremely fast. Such a very sharp growth at the early nucleation stage seems to be very unusual and, to our knowledge,

Figure 16: Temperature dependence of the same temporal characteristics of precipitation as those in Fig. 14, but in terms of the scaled time t_s defined by Eq. (18): t_s^{max} (circles), t_s^c (triangles), and $t_s^{c,0.1}$ (squares). In figure *a*, the states *B*, *D* and *E* have the same $x=1.34$, while solid circle and solid square correspond to experiments [2] for the state *B* with $x=1.34$. In figure *b*, the state *A* corresponds to $x=1.17$; solid circle and solid square at $T=773$ K correspond to the data [6] for the steel NUCu-140 with $x_{Cu}=1.17$; and solid circle at $T=873$ K corresponds to experiments [7] for the state *G* with $x=1.15$.

Figure 17: Numbers of clusters containing k copper atoms, $\nu_k(t)$, observed in our KMC simulations. The first, second, third and fourth row corresponds to the state *G*, *B*, *D* and *F* in Table 1, respectively. Frame G1, G2, G3, or G4 corresponds to the time t equal to $t^{N,0.47}$, t^{max} , $1.1 t^{max}=t^{c,0.87}$, or $t^{c,0.67}$; frame B1, B2, B3, or B4, to $t^{N,0.61}$, t^{max} , $1.1 t^{max}=t^{c,0.94}$, or $t^{c,0.61}$; and frame D1, D2, D3, or D4, to $t^{N,0.6}$, t^{max} , $1.1 t^{max}=t^{c,0.86}$, or $t^{c,0.61}$, respectively, where the time $t^{N,\alpha}$, t^{max} or $t^{c,\alpha}$ is defined by Eq. (23), (20), or (24). Frame F1, F2, or F3 corresponds to the scaled time t_s equal to $t_s^{N,0.48}$, $t_s^{N,0.94}$, or t_s^{max} , where the time $t_s^{N,\alpha}$ is defined by Eq. (23) with replacing $t \rightarrow t_s$, while $t_s^{max} = 1.45$ h corresponds to the end of our simulations for the state *F*.

was never observed in either experiments or simulations, as illustrated by Figs. 5-12. Therefore, the data about $R(t)$ in NUCu-170 at $t=0.25$ h reported in [5] should possibly be taken with some caution.

For the coarsening stage, the results presented in Figs. 5, 8 and 14 fully agree with the main conclusions of Kolli et al. [6] about a very strong slowing down of coarsening in the NUCu steels with respect to binaries Fe-Cu. In particular, the advanced coarsening time $t^{c,0.1}$ for each of these steels exceeds that for its binary analogue by about two orders of magnitude. At the same time, the dependencies of this advanced coarsening time $t^{c,0.1}$ on the copper content x_{Cu} for the NUCu steels and for their binary analogues shown in Fig. 14 seem to be similar.

The strong slowing down of coarsening in a ternary Fe-Cu-Mn alloy with respect to its binary analogue Fe-Cu was also observed by Miller et al. under neutron irradiation [4]. On the contrary, the effects of alloying elements on the nucleation and growth kinetics in Fe-Cu-Mn alloys and in NUCu steels seem to differ qualitatively: according to Figs. 12 and 13, the d_{max} value for an Fe-Cu-Mn alloy is by about twice higher, while for each of NUCu steels, it is by about three times lower than that in its binary analogue. Therefore, for the coarsening stage, the effects of alloying elements on the decomposition kinetics in the multicomponent Fe-Cu-based alloys seem to be much more universal than those for the earlier stages of precipitation.

Such a universal slowing down of coarsening in the multicomponent Fe-Cu-based alloys with respect to their binary analogues Fe-Cu can be related to a significant segregation of alloying elements on the surface of precipitates [4]-[6] which can reduce the surface energy and thereby the thermodynamic driving force for coarsening. It can also be related to a weakening of the vacancy trapping at surfaces of precipitates due to this segregation. However, quantitative estimates of these effects seem to be absent yet.

5 Conclusions

Let us summarize the main results of this work. The earlier-developed *ab initio* model and both the kinetic Monte Carlo (KMC) and the stochastic statistical methods are used to simulate the precipitation kinetics for seven binary Fe-Cu alloys with different copper concentrations x and temperatures T . Comparison of results obtained to available experimental data and to other simulations enable us to make a number of conclusions about kinetic features of precipitation in both the binary Fe-Cu and the multicomponent Fe-Cu-based alloys.

First, we find that due to the strong vacancy trapping by copper precipitates, the precipitation kinetics in iron-copper alloys for all x and T considered differs notably from that observed for the alloys with no such trapping: the “pure nucleation” and “pure growth” stages are relatively short, the nucleation, growth and coarsening stages significantly overlap, while the intermediate “pre-coarsening” stage observed in some simulations for simplified alloy models (illustrated by Fig. 3 of this work and by Fig. 1 in Ref. [20]) is absent. In this connection, the presence of this pre-coarsening stage in simulations of precipitation in irradiated Fe-Cu alloys made by Barashev et al. [21] can be related just to some oversimplifications of their model.

The concentration and temperature dependencies of the maximum precipitate density d_{max} , the nucleation time t^{max} , and the advanced coarsening time $t^{c,0.1}$ defined by Eqs. (20) and (22) are illustrated by Figs. 13-16. At low supersaturations s , these dependencies are rather sharp and seem to be mainly determined by the variations of supersaturation $s(x, T)$ with x or T . At higher $s \gtrsim 0.3$, these temperature dependencies become more smooth and seem to be determined by an interplay between an enhancement with lowering T of both the thermodynamic driving forces promoting the evolution and the vacancy-copper atom correlations reducing the copper diffusivity D_{Cu} and thereby slowing down the evolution.

Temporal evolution of the precipitate size distributions $\nu_k(t)$ is illustrated by Fig. 17. These distributions are typically rather broad, and they strongly vary with the evolution time t . Therefore, the conventional description of these sizes in terms of the mean precipitate size $R(t)$ is oversimplified and incomplete. We also find that for the alloy state G with a relatively high temperature $T=873$ K, the size distribution $\nu_k(t)$ is much more uniform than those observed for the states B and D with the lower temperatures $T=773$ K and $T=713$ K, particularly for the coarsening stage.

We also describe an improved version of the earlier-suggested stochastic statistical method for simulations of precipitation and show that this version can be used for various extrapolations of KMC simulations, in particular, for their extensions to the first stages of coarsening for which the KMC simulations are time-consuming.

Comparison of our simulated temporal dependencies for the density and the mean size of precipitates in binary Fe- x Cu alloys at $x=1.34$, $T=773$ K and $x=1.15$, $T=873$ K to the available experimental data [1, 2, 3, 7] shows a reasonable agreement within both statistical errors of simulations and the scatter of experimental results. The sizes N_c of critical precipitates calculated by the statistical method of Dobretsov and Vaks [14] and presented in Table 1 are close to those estimated in our KMC simulations and in experiments by Kolli et al. [5, 6] for the NUCu steels.

Comparison of results of our simulations for the Fe-1.17Cu and Fe-1.82Cu alloys to the data by Kolli et al. [5, 6] about precipitation in NUCu-140 and NUCu-170 steels which have the same copper content, $x_{Cu} = 1.17$ and $x_{Cu} = 1.82$, and contain the similar amount of other alloying elements enables us to assess the effects of these alloying elements on the

precipitation kinetics. The maximum precipitate density d_{max} in each of these two steels is lower than that in its binary analogue by about three times. For the nucleation stage, the precipitate density $d_p(t)$ and their mean size $R(t)$ observed by Kolli et al. [6] in the NUCu-140 steel seem to be close to those simulated for the Fe-1.17Cu alloy, contrary to the case of the NUCu-170 steel for which the $d_p(t)$ and $R(t)$ values at $t=0.25$ h reported by Kolli and Seidman [5] sharply disagree with those simulated for the Fe-1.82Cu alloy. In this connection we note that the $R(0.25h)=R_{KS}$ value reported in [5] seems to be unrealistically large for the early nucleation stage supposed by Kolli and Seidman for the NUCu-170 steel at $t=0.25$ h: $R_{KS} \simeq 4R_c$. Therefore, further experimental studies of the nucleation kinetics in Fe-Cu-based steels seem to be desirable.

For the coarsening stage, the presence of alloying elements in the NUCu steels leads to a very strong slowing down of coarsening, by 1-2 orders of magnitude, as compared to their binary analogues. A similar strong slowing down of coarsening was also observed by Miller et al. [4]) for an irradiated ternary Fe-Cu-Mn alloy. At the same time, for the nucleation and growth stages, the effects of alloying elements on the maximum precipitate density d_{max} in the NUCu steels and in the Fe-Cu-Mn alloy studied by Shabadi et al. [7] seem to be qualitatively different. Some hypotheses about a possible origin of the universal slowing down of coarsening in multicomponent Fe-Cu-based alloys with respect to their binary analogues are suggested.

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